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Effects of Sulfuric Acid Rain on Major Cation and Sulfate Concentrations of Water Percolating Through Two Model Hardwood Forests

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Effects of Sulfuric Acid Rain on Major Cation and Sulfate Concentrations of Water Percolating Through Two Model Hardwood Forests[1]

JEFFREY J. LEE AND DAVID E. WEBER[2]

ABSTRACT

Acid precipitation falls on vast areas of forested land, including most of the eastern deciduous forest of the United States. Forest productivity, ground-water quality, and surface waters might all be affected. To document and quantify ecosystem response to the onset of acid precipitation, simulated sulfuric acid (H_2SO_4) rain was applied to model forest plots of sugar maple (*Acer saccharum* Marsh.) and red alder (*Alnus rubra* Bong). One set of four plots (two alder and two maple) received a control rain consisting of a stock solution equilibrated with atmospheric CO_2 to approximately pH 5.7. For three sets of four plots, sufficient H_2SO_4 was added to the stock solution to lower the pH to 4.0, 3.5, or 3.0. Nozzles were used to apply simulated acid rain at the rate of 2.8 mm/hour (maple) or 3.7 mm/hour (alder) for 3 hours/day, 3 days/week, throughout the year. Water samples were collected above and below the canopy, below the litter layer, and from 20-cm and 1-m depths below the surface of the soil.

While constituents of the throughfall were similar to those of the simulated rain, the litter leachate (the actual input to the soil) had consistently higher concentrations of SO_4^{2-}, Ca^{2+}, and Mg^{2+}, and higher pH, than the acid rain.

For the first 6 months, SO_4^{2-} adsorption by the soil prevented any apparent differences in the SO_4^{2-}, Ca^{2+}, or Mg^{2+} concentrations or the pH of samples taken from a depth of 20 cm from plots receiving either acid or control treatments. Then, SO_4^{2-} concentrations at this depth on plots receiving the most acidic rain (pH 3.0) became increasingly higher than on the other plots until, after 3 years, they were approximately equal to SO_4^{2-} concentrations in the rain. Soil solutions from the pH 3.5 and 4.0 treatments responded similarly starting 10 months and 1 year, respectively, after initiation of exposure to acid rain. Increased Ca^{2+}, Mg^{2+}, and, to a lesser extent, K^+ concentrations and lowered pH in solutions from the 20-cm depths occurred simultaneously with increased SO_4^{2-} concentrations. At a depth of 1 m, no acid-rain-related effects were evident after 2.5 years exposure to pH 3.0 H_2SO_4 rain. Results showed that a hardwood canopy and litter layer can alter the input of chemicals to the soil from acid rain, that the relative sensitivity of ions to mobilization by acid rain is not the same for all components of an ecosystem, and that acid rain can alter the chemical composition of water within the root zone within a few years, even if the soil is a strong sulfate adsorber.

Additional Index Words: **leaching, nutrient cycling, trees, water pollution, throughfall, soils, ground water.**

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Rainfall over vast areas of Europe and North America has become increasingly acidic (1, 2, 21, 22, 34). The increased acidity of precipitation is primarily due to higher concentrations of sulfuric (H_2SO_4) and nitric (HNO_3) acids derived from the air pollutants sulfur dioxide (SO_2) and oxides of nitrogen (NO_x). Although precipitation may be acidified by a local emission source, transport over hundreds and even thousands of kilometers is common. Acid precipitation thus tends to be regional and chronic (1, 2, 21, 22, 34). With the projected increase in use of fossil fuels, precipitation will probably continue to be acidic. Currently, all states east

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of the Mississippi River regularly receive precipitation that is more acidic than the expected value of pH 5.7 for pure water in equilibrium with atmospheric CO_2 (21, 22). In the northeastern United States, pH 4.2 is typical of winter precipitation; for summer rains, half the events are at pH 4.0 or lower (22). Acid precipitation is not limited to the east, but also occurs in the western U.S. (17, 23, 25).

The impact of acid precipitation on agricultural and forest ecosystems is not well-understood. The potential effects of chronic exposure of forest soils to acid precipitation have been identified as a major concern since, compared with agricultural soils, forest soils are relatively unmanaged (9, 11, 35, 38). Increased anion loading of forest soils implies an increase in cationic concentrations, including basic cations (Ca^{2+}, Mg^{2+}, K^+, Na^+, commonly referred to as "bases" in soil science) and H^+. Thus, increased leaching of bases and acidification of soil solution are immediate consequences of increased anionic input, provided the anions remain in solution. Unless the input of bases also increases, the inbalance of inputs and outputs will eventually lead to acidification of the soil per se, i.e., a decrease in base saturation (11, 14, 31, 33, 34, 36, 37).

Since, by definition, acid rain contains a significant excess of acidic anions over basic cations, both short-term acidification of soil solution and long-term acidification of soil might occur. However, immobilization of anions or mobilization of basic cations by biotic or abiotic ecosystem components could ameliorate the situation. For example, increased mineral weathering might offset losses of changeable bases. Although increased leaching of bases and acidification of soils and mobilization of Al by acid rain have been observed (1, 4, 6, 7, 28), so has increased mineral weathering (3, 15, 27).

Before reaching the forest soil, precipitation percolates through the forest canopy and litter layer. Throughfall from canopies of deciduous trees (1, 8, 12, 24, 26, 39, 40) and leachates from hardwood litter layers (10) tend to have higher pH values; higher Ca^{2+}, Mg^{2+}, K^+, and Na^+ concentrations; and lower volumes than incident acid precipitation. Any study of the effects of acid precipitation on forest soils must consider the differences in quality and quantity between precipitation and the litter leachate, the actual input to the soil. Similarly, any study of biological processes in forest litter or soil must consider the chemical environment provided by the litter leachate or soil solution. It is primarily these solutions that control soil biological processes, including root uptake and, thus, plant growth.

At EPA's Environmental Research Laboratory in Corvallis, Oregon, we used two types of model hardwood forest ecosystems (18, 19) to study the effects of simulated H_2SO_4 rain on nutrient cycling. The objective was to document and quantify ecosystem response to the onset of acid rain. Although simplified, the model forests had many of the interacting components of real forests. As part of this study, for more than 3 years we regularly collected rainwater from above and below the canopy, and leachate from below the litter layer and from two depths in the soil. In this paper, we report on changes in pH, Ca^{2+}, Mg^{2+}, K^+, and SO_4^{2-} in acid rain as it percolated through the ecosystems.

METHODS AND MATERIALS

Each of 18 lysimeter plots arranged in a single east-west line consisted of a 1.5 by 1.5 by 1.2 m water-tight enclosure constructed of fiberglass-covered plywood and filled to a depth of 1.1 m with a forest soil. The soil (Bohannon series of the fine-loamy, mixed, mesic family of Typic Halpumbrepts) was obtained from the Siuslaw National Forest, Oreg., and formerly had supported a red alder (*Alnus rubra* Bong)–Douglas-fir (*Pseudotsuga menziesii* (Mirbel) Franco) community. The horizons were reconstituted with respect to litter, topsoil, and subsoil layers. Each layer was mixed to minimize interplot differences. Soil properties are summarized in Table 1.

In 1975, 36 tree seedlings were planted in each system. Sugar maple (*Acer saccharum* Marsh.) was planted in the first nine of the 18 plots, and red alder in the other 9 plots. Because of excessive growth, maples were pruned to a standard height in June 1977 and July 1978. Alder were pruned in June 1976 and replanted in May 1977 and April 1978. The model ecosystems also contained herbs and ferns brought in with the forest soil. Insects and tree frogs were observed on all plots. Each plot initially received litter obtained from natural tree stands of the corresponding species. Subsequently, leaf fall was collected from each plot and placed on the soil.

Each plot, protected from ambient rain, received simulated acid rain at one of four acidities; there were two plots per treatment. All plots received a stock solution approximating non-acidic rain containing 11 μeq/liter Ca^{2+} (0.22 mg/liter), 12 μeq/liter NH_4^+ (0.22 mg/liter), 5 μeq/liter Na^+ (0.12 mg/liter), 2 μeq/liter K^+ (0.08 mg/liter), 5 μeq/liter Mg^{2+} (0.06 mg/liter), 11 μeq/liter SO_4^{2-} (0.53 mg/liter), 12 μeq/liter NO_3^- (0.74 mg/liter), and 12 μeq/liter Cl^- (0.43 mg/liter). These concentrations were based on a 7-year average from Hubbard Brook, N.H. (20), after elimination of estimated H_2SO_4 and HNO_3 components. One set of four plots (two alder and two maple) served as controls, receiving only the stock solution equilibrated with atmospheric CO_2 to approximately pH 5.7. For three sets of four plots, sufficient H_2SO_4 was added to the stock solution to lower the pH to 4.0, 3.5, or 3.0. One plot on each end of the row of plots received only deionized water, and served as a buffer plot. Plots 2–5 received pH 3.0, 5.7, 3.5, and 4.0 rain treatments; this pattern was repeated for the remaining 12 treatments. Nozzles were used to apply rain at the rate of 2.8 (maple) or 3.7 mm/hour (alder) for 3 hours/day and 3 days/week throughout the year. Annual rain amounts (131 cm for maple and 173 cm for alder) approximated those of areas in which these species usually grow. Application of the rain began the last week of June 1976 and ended the first week of January 1980. Rain was interrupted from 6 Dec. 1977 to 16 Feb. 1978 (eliminating 32 scheduled rain events) due to winter damage to equipment. Severe freezing temperatures also prevented nine scheduled rain applications during the winter of 1978–1979.

The plots were located under a transparent (90% transmittance) roof open on the ends and sides. Shade cloths (73% shade) were positioned over the plots during simulated rain events. The plots were thus subjected to near-ambient temperature, relative humidity, and light intensity, except during simulated rain events. Although not measured, dry deposition was probably less than ambient. The facility is located on the Schmidt Research Farm of Oregon State University, near Corvallis.

Polypropylene beakers and funnels were used to collect biweekly rain and throughfall samples for chemical analysis. Ceramic candles (Soil Moisture Equipment Corp.[1]) were joined to form 1.3-m tubes; seven such tubes were placed parallel to each other 10 cm above the bottom of each plot (100 cm below the soil surface) and connected to a 19-liter (5-gal) glass carboy (Kimble) above the soil. Two 30-cm ceramic candles were placed 23 cm below the soil surface (level 2 in Table 1) and connected to a 500-ml polypropylene filtering flask; after the soil settled, these were approximately 20 cm below the surface. Porous ceramic disks (Coors) were cemented to polypropylene funnels and placed so that the disks were slightly above the soil surface in the litter layer; the funnels were connected to 500-ml polypropylene filtering flasks. All tubing and fittings were polypropylene and stoppers were Vikem.

Litter leachate and 20-cm soil solution were sampled biweekly for chemical analysis by applying vacuum to the filtering flasks. To pre-

[1]Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Table 1—Chemical analyses of soil used in lysimeter studies.

Level	Original depth	Salts	Organic matter	Total-N	NO_3-N	Zn	SO_4-S	P	Exchangeable bases				CEC	Reaction
									K	Ca	Mg	Na		
	cm	mmhos/cm	%	mg/kg					meq/100 g					pH
1	0–20	0.22	11.1	0.30	15.4	–	–	10	0.52	1.0	0.43	0.07	31.5	4.8
2	20–40	0.28	8.1	0.24	24.1	0.25	7.8	7	0.65	2.2	0.93	0.17	33.0	5.2
3	40–50	0.20	8.1	0.26	16.9	0.14	7.4	5	0.56	0.9	0.40	0.12	37.7	4.8
4	50–60	0.13	3.9	0.15	11.1	0.09	12.0	4	0.35	0.6	0.40	0.10	30.7	5.0
5	60–110	0.10	2.0	0.08	4.1	0.09	20.4	3	0.29	0.6	0.74	0.11	30.6	5.0

vent soil saturation, vacuum was applied to the ceramic tubes at 100-cm depth whenever water could be drawn from the soil; vacuum application was essentially continuous during winter. Every 4 weeks, aliquots of the 1-m soil solution were taken for chemical analysis. In addition to pH, Ca^{2+}, Mg^{2+}, K^+, Na^+, and SO_4^{2-}, samples were analyzed for Cl^-, ortho-phosphate (PO_4^-), NO_3^-, NH_4^+, Kjeldahl N, organic C, and trace metals (Al, Fe, Mn, and others).

In order to quantify response, data were fit to linear-regression equations of the form:

$$\ln y = B_0 + B_1 \ln x + B_2 (\ln x)^2, \quad [1]$$

where x and y were ionic concentrations of the various solutions. The data were ln-transformed to produce cumulative-frequency distributions closer to normal distributions than for the untransformed data. Since pH is logarithmic, it was entered directly into equations. B_1 was accepted into an equation only if the F-value for inclusion was at least 3.0. B_2 was accepted only if the F-criterion was met and if the resulting increase in R^2 was at least 0.05. Both requirements were imposed to eliminate instances where, because of the large number of data points (300–500) in each analysis, large F-values were associated with extremely small changes in R^2. Non-linear regression equations (negative exponential, logistic) were also tried. Since these resulted in essentially the same values of R^2, they provided no advantages over linear regression analysis and were not used.

Differentiation and rearrangement of Eq. [1] yields

$$\left(\frac{x}{y}\right)\left(\frac{dy}{dx}\right) = B_1 + 2B_2 \ln x. \quad [2]$$

A similar result, with ln x replaced by pH, is obtained when x and y are H^+ concentrations. The left-hand side of Eq. [2] is the *relative sensitivity of y to x*; i.e., the percent change in y expected from a 1% change in x. For equations without B_2, the relative sensitivity is simply given by B_1. Thus, for those cases, B_1 is a measure of the strength of the relationship between x and y. The same value of the relative sensitivity applies if the concentrations are expressed as mass, moles, or equivalents per liter.

The time-behaviors of pH and of Ca^{2+} and Mg^{2+} concentrations in the 20-cm soil solution and of pH in the 1-m soil solution were also examined. Time (t)-dependent terms of the form t, t^2, sin ($2\pi nt/52$), and cos ($2\pi nt/52$) (n = 1, 2, 3) were tentatively added to Eq. [1], where t is in weeks. The sine and cosine terms for each value of n were added in pairs as a check for periodic (e.g., seasonal) responses. This is algebraically equivalent to including terms of the form B_n sin ($[2\pi nt/52] + \phi_n$), but avoids non-linear regression analysis.

The order in which time-dependent terms were added was not forced, but chosen to maximize increases in R^2. They were included only if they met the F and R^2 criteria described above. This resulted in the inclusion of t-dependent terms in the equations for pH; no t-dependent terms were added to the equations for Ca^{2+} and Mg^{2+}. None of the sine or cosine terms were included.

Measured SO_4^{2-} concentrations were used to obtain predicted-time curves for Ca^{2+} and Mg^{2+} concentrations and for pH of the 20-cm soil solution of the maple plots. First, an average SO_4^{2-} concentration was obtained for each treatment pair for each sampling period (i.e., every 2 weeks). These values (and time, for pH) were entered into the regression equations to obtain predicted cation concentrations for each rain treatment for the maple plots. When graphed vs. time, the results reflected the stochastic nature of the input variable, SO_4^{2-}. The degree of randomness was reduced by drawing a smooth curve through the majority of the predicted values. These curves were then superimposed on graphs of data vs. time.

RESULTS

Changes in Ca^{2+}, Mg^{2+}, K^+, and SO_4^{2-} concentration and in pH of water after percolation through various layers are summarized in Table 2 for alder and maple plots. Since graphs of the Na^+ data did not indicate any treatment or time effects, no statistical analysis of Na^+ was performed; concentrations of Na^+ were generally < 1 mg/liter. Some of the maple plot results are shown in Fig. 1–5. Throughout this set of figures, the same set of symbols is used to indicate the four rain-pH treatments. Regression curves based on Eq. [1] are also shown.

Since they are very similar to results from the maple plots (Fig. 1–5), graphs of results from the alder plots are not shown. Data from these plots for the first 3 years are shown in Lee and Weber (19), as are additional graphs of data from the maple plots. Note, however, that the values given in Table 2 are the results of linear-regression analysis of all maple and alder data.

Throughfall

Figure 1 shows pH of throughfall vs. rain. For both pH and SO_4^{2-}, results fell close to the line of equality, concentration in rain equals concentration in throughfall ($y = x$), for both alder and maple plots (Table 2, Fig. 1). For example, for a rain pH of 4.0, the regressions predict a throughfall pH of 4.1 for both tree species. The high values for R^2 (0.90–0.94) and B_1 (0.91–0.96) show the high degree of dependence of throughfall values on rain values. The tendency towards increased leaching of Mg^{2+}, Ca^{2+}, or K^+ with increased SO_4^{2-} concentration was quite small for alder and maple plots as shown by the small values of R^2 and B_1 (Table 2).

Litter Leachate

The pH of water that had percolated through the litter is plotted against the pH of the incident rainwater in Fig. 2. For all H_2SO_4 treatments, the pH of the litter leachate was considerably higher than the pH of the incident rain, indicating that the litter partially neutralized the acid. This effect was stronger for alder litter than for maple litter (Table 2); for a rain pH of 4.0, the regression equations predict litter leachate pH values of 5.42 (alder) and 5.05 (maple). For plots receiving control rain (pH 5.7), the pH of the litter leachate typically was somewhat less than the pH of the rain for alder (pH 5.35 predicted by regression equation) and somewhat higher for maple (predicted pH 5.92).

Table 2. Results of regression analyses. Equations were of the form $\ln y = B_0 + B_1 \ln x + B_2 (\ln x)^2$, except that pH was not transformed (see text). Units (except for pH) are mg/liter. For soil-solution pH, time (t) in weeks was also used. Unless otherwise noted, x and y were from same ecosystem level.

Level	y	x	$B_0 \pm$ SE	$B_1 \pm$ SE	$B_2 \pm$ SE	R^2
			Maple			
Throughfall	pH	pH (rain)	0.20 ± 0.05	0.96 ± 0.01		0.942
	SO_4	SO_4 (rain)	0.31 ± 0.05	0.91 ± 0.02		0.901
	Mg	SO_4	−1.89 ± 0.14	0.19 ± 0.05		0.065
	Ca	SO_4	−1.20 ± 0.12	0.31 ± 0.04		0.145
	K	SO_4	−0.76 ± 0.20	0.26 ± 0.07		0.056
Litter	pH	pH (rain)	−6.79 ± 0.38	4.68 ± 0.18	−0.43 ± 0.02	0.878
	SO_4	SO_4 (rain)	0.18 ± 0.05	1.01 ± 0.02		0.896
	Mg	SO_4	−0.74 ± 0.06	0.27 ± 0.02		0.291
	Ca	SO_4	0.35 ± 0.04	0.39 ± 0.01		0.620
	K	SO_4	0.39 ± 0.16	0.19 ± 0.05		0.031
Soil (20-cm)	pH	SO_4	7.13 ± 0.07	−0.47 ± 0.03		0.383
	Mg	SO_4	−2.22 ± 0.07	0.93 ± 0.03		0.718
	Ca	SO_4	−1.23 ± 0.06	0.86 ± 0.03		0.709
	K	SO_4	−1.09 ± 0.11	0.29 ± 0.04		0.106
	Ca	Mg	0.82 ± 0.02	0.79 ± 0.02		0.748
	pH	SO_4, t	7.24 ± 0.06	−0.36 ± 0.03, −0.0040 ± 0.0004		0.514
			Alder			
Throughfall	pH	pH (rain)	0.25 ± 0.07	0.96 ± 0.02		0.900
	SO_4	SO_4 (rain)	0.23 ± 0.05	0.93 ± 0.02		0.925
	Mg	SO_4	−1.61 ± 0.16	0.15 ± 0.05		0.043
	Ca	SO_4	−0.88 ± 0.14	0.18 ± 0.05		0.050
	K	SO_4	NS†	NS		NS
Litter	pH	pH (rain)	−8.54 ± 0.50	5.97 ± 0.24	−0.62 ± 0.03	0.726
	SO_4	SO_4 (rain)	0.29 ± 0.05	0.96 ± 0.02		0.903
	Mg	SO_4	−1.19 ± 0.20	1.01 ± 0.15	−0.14 ± 0.03	0.236
	Ca	SO_4	0.39 ± 0.07	0.37 ± 0.02		0.437
	K	SO_4	NS	NS		NS
Soil (20-cm)	pH	SO_4	6.66 ± 0.08	−0.41 ± 0.03		0.417
	Mg	SO_4	−1.56 ± 0.10	0.76 ± 0.04		0.579
	Ca	SO_4	−0.60 ± 0.08	0.78 ± 0.03		0.660
	K	SO_4	−0.72 ± 0.11	0.10 ± 0.04		0.018
	Ca	Mg	0.93 ± 0.02	0.86 ± 0.02		0.827
	pH	SO_4, t	6.80 ± 0.08	−0.35 ± 0.08, −0.0029 ± 0.0006		0.468

† NS = not significant.

The regression curve given in Table 2 predicts little difference in the pH of litter between alder plots receiving either pH 4.0 or control rain (pH 5.43 vs. pH 5.35). It also predicts a maximum litter leachate pH of 5.8 for a rain pH of 4.8. This peak, which occurs in an interval with very little data, is probably an artifact of the regression analysis, despite the high R^2 values (0.73–0.88); the true curve is probably approaching a plateau of approximately pH 5.5 for rain pH values above 4.0. This could occur if the litter is acting as a buffer in this region.

The concentrations of SO_4^{2-} in litter leachate and in rain are compared in Fig. 3. The line of equality, $y = x$, is also shown. For both alder and maple the concentrations were generally greater in the litter leachate than in the corresponding acid rain (Fig. 3, Table 2). This tendency was most pronounced for maple, especially for the pH 3.0 rain treatment. For this treatment SO_4^{2-} concentration (from the regression equations) was 25% greater in litter leachate than in rain for maple, and 15% greater for alder. The high values of R^2 (0.90) and B_1 (0.96–1.0) are similar to those found for SO_4^{2-} in throughfall (Table 2).

Although the data were highly variable, there was a tendency towards increased leaching of Ca^{2+} and Mg^{2+} from the maple litter layer with increased SO_4^{2-} concentrations (Table 2). The higher values of R^2 and B_1 indicate that this tendency was greater for the litter than for the canopy, and greater for Ca^{2+} than for Mg^{2+}. The second-order regression for Mg^{2+} in alder plots (Table 2) has a relative sensitivity of 0.6 at a SO_4^{2-} concentration of 5 mg/liter, decreasing to about 0.06 at 50 mg/liter. Potassium concentrations were only slightly sensitive to differences in SO_4^{2-} concentration for maple litter, and insensitive for alder litter (Table 2).

Shallow Soil Solution

Figure 4 shows the temporal variation of SO_4^{2-}, Mg^{2+}, Ca^{2+}, and pH in solution 20 cm below the soil surface. Week 1, the last week in June 1976, was the first application of acid rain. During week zero, all plots received control rain. Inspection of Fig. 4 as well as theoretical considerations (14, 31, 36, 37), suggested that the sequence of SO_4^{2-} concentrations governed the sequence of Ca^{2+} and Mg^{2+} concentrations. Thus, we sought statistical relationships among these ions (Table 2), and used these to predict the Ca^{2+} and Mg^{2+} time curves from the SO_4^{2-} data. As discussed above, these curves, shown in Fig. 4, were obtained by entering the average SO_4^{2-} concentrations for each treatment and sample period into the regression equations and then smoothing the

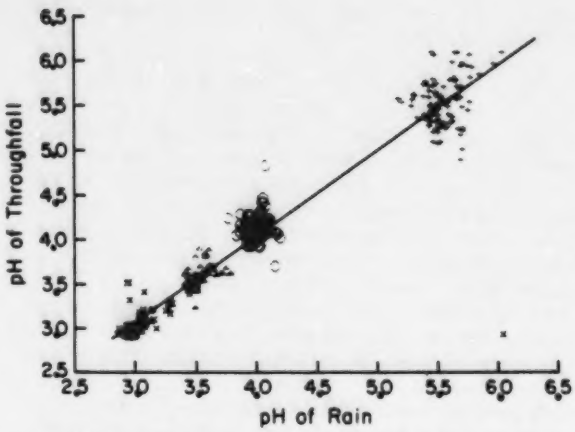

Fig. 1—pH of throughfall vs. pH of rain. Symbols refer to nominal pH of rain treatment: X = pH 3.0, Δ = pH 3.5, ○ = pH 4.0, and + = pH 5.7. Curve represents regression equation of Table 2.

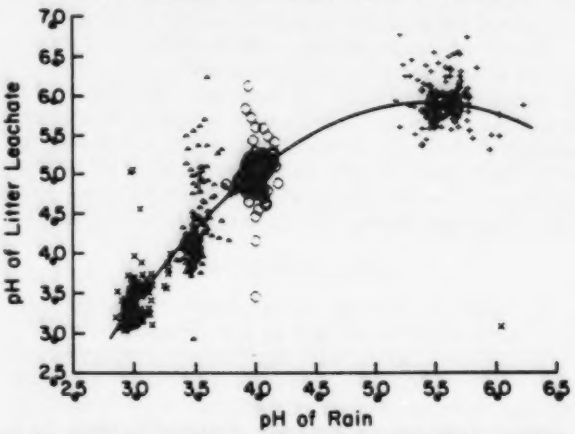

Fig. 2—pH of litter leachate vs. pH of rain. Symbols refer to nominal pH value of rain treatment: X = pH 3.0, Δ = pH 3.5, ○ = pH 4.0, and + = pH 5.7. Curve represents regression equation of Table 2.

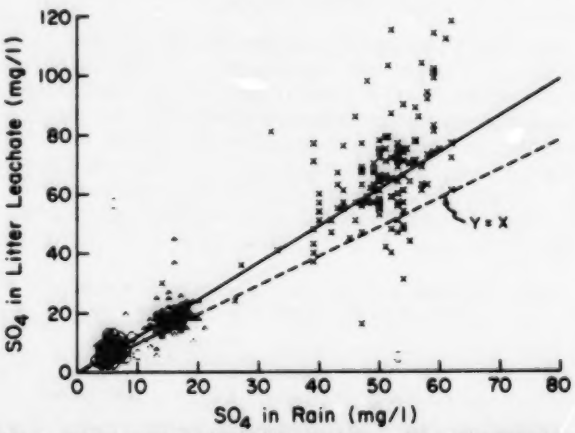

Fig. 3—Sulfate concentration of litter leachate vs. SO_4^{2-} concentration of rain. Symbols refer to nominal pH value of rain treatment: X = pH 3.0, Δ = pH 3.5, ○ = pH 4.0, and + = pH 5.7. Diagonal line represents points at which SO_4^{2-} concentrations of rain and litter leachate would be equal. Curve represents regression equation of Table 2.

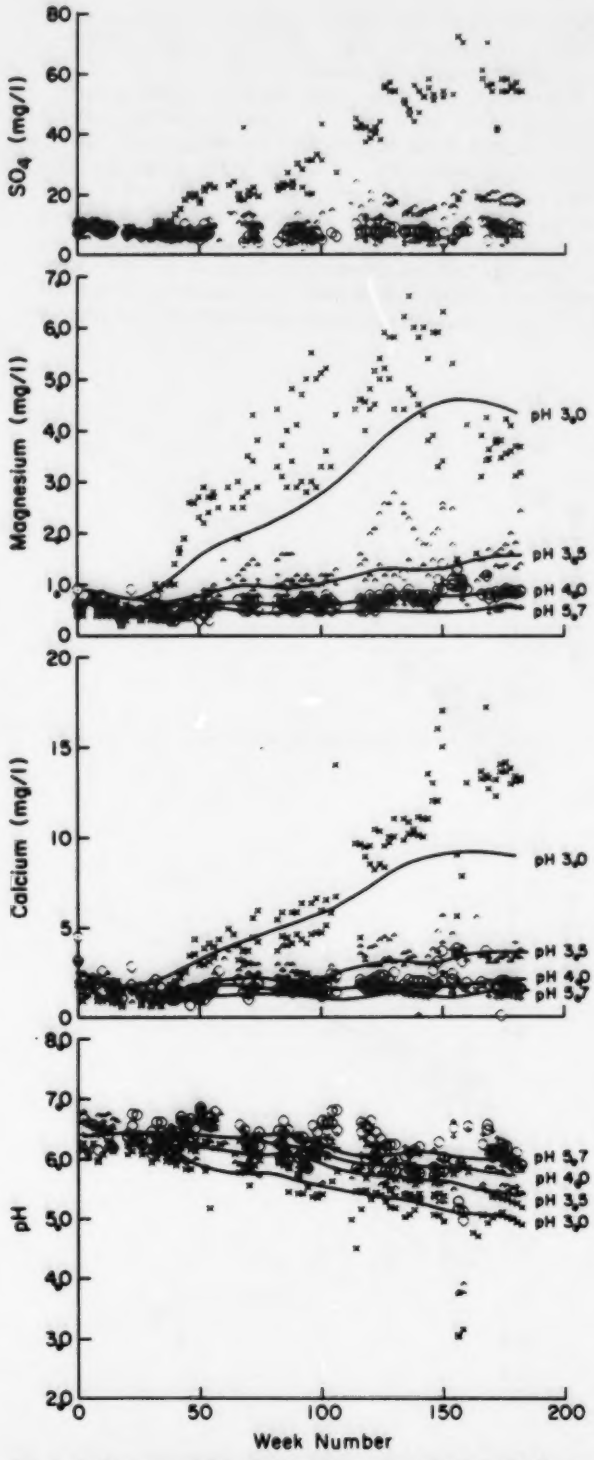

Fig. 4—Sulfate, magnesium, and calcium concentrations and pH of 20-cm soil solution vs. time since beginning of treatment. Symbols refer to nominal pH value of rain treatment: X = pH 3.0, Δ = pH 3.5, ○ = pH 4.0, and + = pH 5.7. Curves were obtained from time-independent (Ca, Mg) or time-dependent (pH) regression equations of Table 2 and SO_4^{2-} data; see text.

results by eye. The time-independent regressions of Table 2 were used for Mg^{2+} and Ca^{2+}; a separate, time-dependent regression was used for pH.

For the first 6 months, there were no apparent differences in SO_4^{2-}, Mg^{2+}, or Ca^{2+} concentrations in 20-cm soil solutions from maple plots receiving acid rain or control treatments (Fig. 4). Then, SO_4^{2-} concentrations from plots receiving the most acid rain (pH 3.0) became increasingly higher than those taken from the other plots. After 3 years, SO_4^{2-} concentrations in the 20-cm soil solution became approximately equal to the concentrations in the rain. Solutions corresponding to the pH 3.5 and 4.0 treatments responded similarly starting 10 months and 1 year, respectively, after the initiation of simulated acid rain exposures.

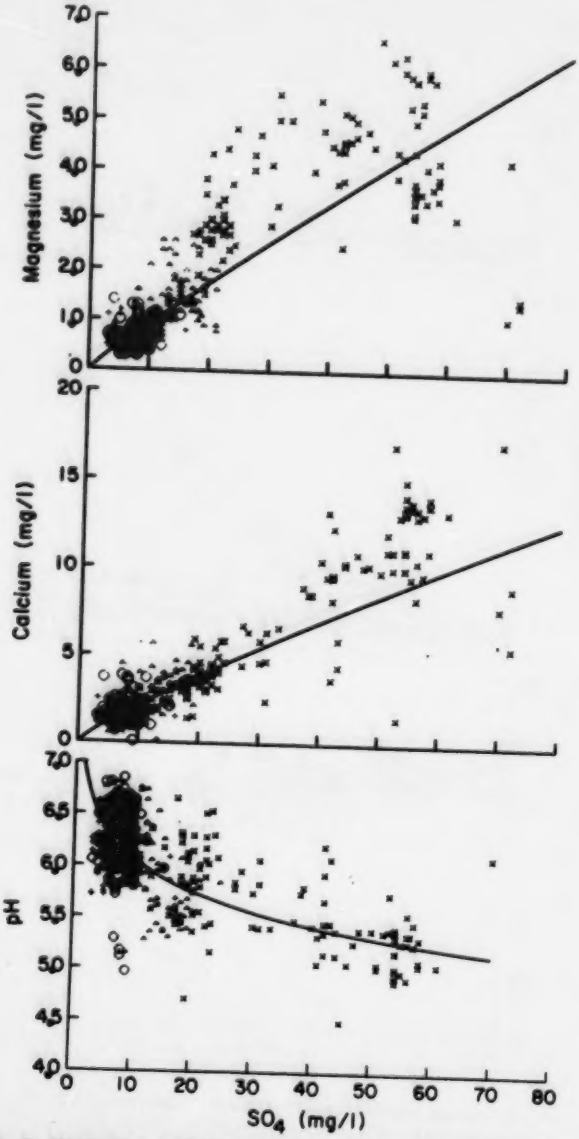

Fig. 5—Magnesium, calcium, and pH vs. SO_4^{2-} concentration of 20-cm soil solution. Symbols refer to nominal pH value of rain treatment: X = pH 3.0, Δ = pH 3.5, ○ = pH 4.0, and + = pH 5.7. Curves represent regression equations of Table 2.

Temporal variation of Mg^{2+} and Ca^{2+} concentrations generally followed the SO_4^{2-} trend (Fig. 4). Figure 5 shows the relationship between SO_4^{2-} concentrations and the concentrations of Mg^{2+} and Ca^{2+}. The high values of R^2 and B_1 (Table 2) indicate a strong relationship between the concentrations of these cations and of SO_4^{2-}. Magnesium and calcium concentrations followed similar trends, and were closely related (Table 2). Potassium concentrations were considerably less sensitive to changes in SO_4^{2-} concentrations (Table 2).

Dry soil conditions (probably due to elevated summer temperatures and vigorous growth) prevented extraction of samples from the 20-cm depth in alder plots during the early part of the experiment. For the period for which samples were taken, the patterns for alder were similar to those for maple (19) (Table 2). However, there was greater scatter of the data points and, especially for Mg^{2+}, an indication of seasonal trends (19). However, none of the time-dependent terms that were tested significantly improved the regression curve.

The pH of the 20-cm soil solution followed a trend toward lower values for both alder and maple plots for all treatments (Table 2); an explicitly time-dependent term was included in these equations. The relationships between H^+ and SO_4^{2-} concentrations were not as strong as for Mg^{2+} and Ca^{2+} (Fig. 5). However, after 3.5 years, 20-cm soil solution from pH 3.0 treatment plots was 0.8–1.0 pH units lower than from control plots (Fig. 4).

Deep Soil Solution

No acid-rain-related effects were observed for solutions taken from a depth of 1 m. The pH vlaues for the maple plots did not vary significantly during the 3.5 years ($R^2 = 0.0004$). There was a slight downward trend of 0.0028 pH units/week in the alder plots ($R^2 = 0.077$). Sulfate concentrations generally remained below 3 mg/liter for all maple and alder plots.

DISCUSSION

Eaton et al. (8) determined throughfall chemistry in a sugar maple stand receiving ambient acid rain (pH 4.1). Their results for Ca^{2+}, Mg^{2+}, and SO_4^{2-} (Table 3) indicated that partial neutralization occurred in the canopy, and that throughfall was considerably enriched in Ca^{2+}, Mg^{2+}, K^+, and SO_4^{2-}, compared with incident precipitation. These effects were more pronounced for trees with 40- to 65-cm dbh (diameter breast height) than for trees with 15- to 25-cm dbh. For rain at pH 4.1 (SO_4^{2-} concn,

Table 3—Chemical content of precipitation and throughfall in a sugar maple stand [adapted from Eaton et al. (8)].

	Precipitation	Throughfall	
		Small trees (15–24 cm dbh)	Large trees (40–65 cm dbh)
	mg/liter		
Ca^{2+}	0.16	1.13	1.58
Mg^{2+}	0.03	0.37	0.40
K^+	0.07	3.81	8.03
SO_4^{2-}	2.7	16.4	25.2
pH	4.1	4.6	4.9

3.8 mg/liter), our regression equations (Table 2) predict Ca^{2+}, Mg^{2+}, K^+, and SO_4^{2-} concentrations of 0.46, 0.19, 1.9, and 4.59 mg/liter, and a pH value of 4.14, for maple throughfall. Thus, rainwater was less enriched in these ions by the canopy in our study than by a true forest canopy. This might reflect the smaller size of the maple trees (< 5-cm dbh) used in our study, or differences in dry deposition.

When Fairfax and Lepp (10) exposed maple (*Acer pseudoplatanus*) leaf litter to simulated H_2SO_4 rain at pH 4.0, the resultant leachate had a pH of 5.2. Calcium concentration in this leachate was 13 times that in leachate from litter exposed to deionized water (pH 6.8); similar results were obtained for the other hardwood litters they tested. We also found significant neutralization of H_2SO_4 acid by litter (Fig. 2, Table 2), and that higher Ca^{2+} concentrations (Table 2) were associated with the more acidic treatments. Thus, when acid rain falls on a hardwood forest with a well-developed canopy and litter layer, the actual input to the soil will probably be considerably less acid than the incident precipitation. Also, precipitation that is more acid will cause more rapid leaching of cations from canopy and litter into the soil. These effects could, for at least a few years, tend to offset any leaching of cations from the soil.

Cronan et al. (5) observed average SO_4^{2-} concentrations of 8 mg/liter in soil solutions beneath a coniferous forest in New England; they attributed 76% of cation leaching from the soil to the presence of SO_4^{2-} anion. For solutions obtained from beneath a hardwood forest subject to acid rain, Koterba et al. (16) observed an average SO_4^{2-} concentration of 5 mg/liter. In both cases, the soils had been exposed to H_2SO_4 rain for approximately 30 years, and to non-acidic SO_4^{2-} rain for considerably longer. Thus, the ability of the soil to absorb SO_4^{2-} probably had been exhausted. While soil solutions in areas which had only recently begun to receive H_2SO_4 rain might not show an immediate response to increased SO_4^{2-} loadings, the response to HNO_3 rain could be more rapid (13, 14, 31). However, since most forests are N-limited, biological uptake could tie up most available N. Thus, less NO_3^- would be available for leaching, at least during the growing season. Ultimately, decomposition of this organic material would release H^+, contributing to leaching (30).

The soil used in our experiment was a strong SO_4^{2-} adsorber (14). Figure 4 demonstrates a breakthrough phenomenon as the SO_4^{2-} adsorption capacity of the soil was approached. As expected from the theoretical work of Wiklander (36, 37), Johnson and Cole (14), and Reuss (31), increased anion concentrations caused increased concentrations of Ca^{2+} and Mg^{2+} and lowered pH in the soil solutions (Fig. 4); however, changes in K^+ concentrations were unexpectedly low. Cronan (4) and Singh (32) also found that K^+ concentrations responded to increased SO_4^{2-} concentrations differently than did Ca^{2+} or Mg^{2+}. Cronan (4) attributed the lack of increased mobility of K^+ with increased SO_4^{2-} to biological uptake.

Our results thus are consistent with the "mobile anion concept" (14, 31). According to this theory, the observed changes in cation concentrations were not necessarily due to changes in the base saturation of the soil, but were probably the result of increased ionic strength of the soil solution. The increased scatter of data on cation concentrations for alder plots compared with maple plots was possibly due to variable NO_3^- concentrations associated with symbiotic N fixation, a characteristic of the genus *Alnus*. Overrein et al. (29) also concluded that the mobile anion concept can explain changes in cation mobility in forest soils. Cronan (4) and Singh (32) also emphasized the importance of SO_4^{2-} mobility for cation transport.

Although the "sulfate front" presumably had moved downwards into the soil, it had not reached a depth of 1 m; no effects attributable to acid rain were observed in solutions extracted from this depth. Increased SO_4^{2-} concentrations in throughfall and litter leachate, compared with rain, could accelerate downward movement of the SO_4^{2-} front.

CONCLUSION

In summary, these results show that interaction with a well-developed hardwood canopy and litter layer can significantly raise the pH and increase concentrations of basic cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) in rainwater; SO_4^{2-} concentrations can also be increased. Increased anion concentrations in soil solutions will cause increased concentrations of cations, generally including both basic cations and H^+. This would immediately lead to increased leaching of basic cations from the soil and to decreased pH of the soil solution. However, H_2SO_4 rain might not cause significantly higher SO_4^{2-} concentrations in soil solutions until the ability of the soil to adsorb SO_4^{2-} is exhausted. Our results suggest that, for a strong SO_4^{2-} adsorber, this might occur after a year or two for rain at pH 4.0. The response of soil solutions to HNO_3 rain could be more rapid, but lower in magnitude. Long-term changes in base saturation would depend on the balance between increased output and possibly altered inputs of Ca^{2+}, Mg^{2+}, Na^+, and K^+.

The regressions of Table 2 can be used with Eq. [2] to rank the major ions by sensitivity to H_2SO_4 rain. For these model ecosystems, we have:

throughfall,

$H^+ \geq SO_4^{2-} > Ca^{2+} > K^+ > Mg^{2+}$ (maple), and

$H^+ \geq SO_4^{2-} > CA^{2+} = Mg^{2+} > K^+$ alder);

litter leachate (pH 4.),

$H^+ > SO_4^{2-} > Ca^{2+} > Mg^{2+} > K^+$ maple), and

$H^+ > SO_4^{2-} > Mg^{2+} > Ca^{2+} > K^+$ alder);

litter leachate (pH 5.),

$SO_4^{2-} > Ca^{2+} = H^+ > Mg^{2+} > K^+$ (maple), and

$Mg^{2+} > SO_4^{2-} > CA^{2+} > H^+$ (alder); and

soil,

$Mg^{2+} \geq Ca^{2+} > H^+ > K^+$ (maple, alder).

Sodium did not appear sensitive to acid rain treatment.

The various layers of the model ecosystems responded differently to H_2SO_4 rain. This result emphasizes that the effects of acid precipitation on forest soils can only be adequately studied in an ecosystem context. Specifically, the following must be considered:

1) changes in rain chemistry caused by passage through canopy and litter layer;
2) effects of altered soil solution chemistry on uptake of chemicals by plants;
3) effects on other soil biological processes such as decomposition, N fixation, nitrification, S oxidation/reduction, and others;
4) effects on weathering of minerals; and
5) role of SO_4^{2-} adsorption by the soil in controlling the chemistry of the soil solution.

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